

Rev's Patent 08 SEP 2004

10/507379

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) BE.02.021 PCT

Box No. I TITLE OF INVENTION

System for Treating an Underground Formation

Box No. II APPLICANT

☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Resolution Research Nederland B.V.
Vondelingenweg 601
NL-3196 KK Vondelingenplaat Rotterdam
the Netherlands

Telephone No.
+32 (10) 477 548

Facsimile No.
+32 (10) 477 552

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BOSSAERTS Jan Dirk
Poenaardlaan 23
B-3090 Overijse
Belgium

This person is:

☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
BE

State (that is, country) of residence:
BE

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☐ agent ☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

Resolution Research Nederland B.V.
Intellectual Property Section
p/a Resolution Research Belgium S.A.
Avenue Jean Monnet 1
B-1348 Ottignies-Louvain-la-Neuve
Belgium

Telephone No.
+32 (10) 477 548

Facsimile No.
+32 (10) 477 552

Teleprinter No.

Agent's registration No. with the Office

☒ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

RANS Marc Jozef
Bovenbosstraat 51
B-3053 Haasrode
Belgium

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
BE

State (that is, country) of residence:
BE

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZM Zambia, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT (if other kind of protection or treatment desired, specify on dotted line)
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, BG Bulgaria, CH & LI Switzerland and Liechtenstein, CY Cyprus, CZ Czech Republic, DE Germany, DK Denmark, EE Estonia, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, SI Slovenia, SK Slovakia, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GQ Equatorial Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | | |
|---|--|---|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> AG Antigua and Barbuda | <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> OM Oman |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> PH Philippines |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> JP Japan | |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> SC Seychelles |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> KR Republic of Korea | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> BZ Belize | <input checked="" type="checkbox"/> KZ Kazakhstan | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> LC Saint Lucia | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> CH & LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> LK Sri Lanka | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> LR Liberia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> CO Colombia | <input checked="" type="checkbox"/> LS Lesotho | <input checked="" type="checkbox"/> TN Tunisia |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> LT Lithuania | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> LU Luxembourg | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> LV Latvia | |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> MA Morocco | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> MD Republic of Moldova | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> MG Madagascar | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> DZ Algeria | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> EC Ecuador | <input checked="" type="checkbox"/> MN Mongolia | |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> MW Malawi | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> MX Mexico | <input checked="" type="checkbox"/> VC Saint Vincent and the Grenadines |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> MZ Mozambique | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> NO Norway | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> GD Grenada | | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> GE Georgia | | <input checked="" type="checkbox"/> ZM Zambia |
| <input checked="" type="checkbox"/> GH Ghana | | <input checked="" type="checkbox"/> ZW Zimbabwe |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) 17th May 2002 17.05.02	02076950.1		EP	
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items
 ☒ item (1)
 ☐ item (2)
 ☐ item (3)
 ☐ item (4)
 ☐ item (5)
 ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA /

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)	Number	Country (or regional Office)
7th October 2002	02076950	EP

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of
declarations

- | | | |
|---|--|---|
| <input type="checkbox"/> Box No. VIII (i) | Declaration as to the identity of the inventor | : |
| <input type="checkbox"/> Box No. VIII (ii) | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | : |
| <input type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv) | Declaration of inventorship (only for the purposes of the designation of the United States of America) | : |
| <input type="checkbox"/> Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : |

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:

(a) **in paper form**, the following number of sheets :

request (including declaration sheets) : 5

description (excluding sequence listings and/or tables related thereto) : 6

claims : 1

abstract : 1

drawings : 1

Sub-total number of sheets : 13

sequence listings :

tables related thereto :

(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)

Total number of sheets : 13

(b) ☐ **only in computer readable form** (Section 801(a)(i))(i) ☐ sequence listings(ii) ☐ tables related thereto(c) ☐ **also in computer readable form** (Section 801(a)(ii))(i) ☐ sequence listings(ii) ☐ tables related thereto

Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the

☐ sequence listings:☐ tables related thereto:

(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)

This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):

1. ☒ fee calculation sheet :
2. ☐ original separate power of attorney :
3. ☐ original general power of attorney :
4. ☒ copy of general power of attorney; reference number, if any: GA.43073. :
5. ☐ statement explaining lack of signature :
6. ☐ priority document(s) identified in Box No. VI as item(s): :
7. ☐ translation of international application into (language): :
8. ☐ separate indications concerning deposited microorganism or other biological material :
9. ☐ sequence listings in computer readable form (indicate type and number of carriers)
- (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) :
- (ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter :
- (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listings mentioned in left column :
10. ☐ tables in computer readable form related to sequence listings (indicate type and number of carriers)
- (i) ☐ copy submitted for the purposes of international search under Section 802(b-quarter) only (and not as part of the international application) :
- (ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quarter) :
- (iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column :
11. ☒ other (specify): Copy Search Report :

Number of items

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

van der STRAATEN Jan Anthony (GA no. 43073)

For receiving Office use only

1. Date of actual receipt of the purported international application:

3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:

4. Date of timely receipt of the required corrections under PCT Article 11(2):

5. International Searching Authority (if two or more are competent): ISA /

6. ☐ Transmittal of search copy delayed until search fee is paid

2. Drawings:

☐ received:☐ not received:

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

Final Version.

SYSTEM FOR TREATING AN UNDERGROUND FORMATION

5 The present invention relates to a method of treating an underground formation. More in particular, the present invention relates to a method of treating an underground formation in oil and gas reservoirs, by using a consolidation solution of an epoxy resin and a curing agent. Such a method was known from e.g. EP 0864032 B1, which actually disclosed a method of treating an underground formation comprising the sequential steps of

- 10 (a) contacting the formation with an aqueous medium;
- (b) contacting the formation with a hydrocarbon fluid;
- (c) contacting the formation with a solvent in the form of a glycol ether;
- (d) contacting the formation with a consolidation solution comprising a monomeric diglycidyl ether of bisphenol A, such as EPIKOTE 828, in a proportion of from 30 to 60 %m and methylene
- 15 dianiline as curing agent in a proportion of from 5 to 20 %m in the solvent and
- (e) contacting the formation with a viscosified hydrocarbon fluid (the so called over-flush) to displace a majority of the resin phase and to restore the permeability of the treated underground.

As suitable glycol ethers for the solvent were exemplified methoxy propanol, butoxyethanol, hexoxy ethanol and isomers of these glycol ethers, which may be optionally mixed with a minor amount (e.g.

20 less than 10 %m) of a polyethylene glycol, having an average molecular mass of around 400, to adjust the viscosity.

It is true that on the other hand was known from 'Journal of Petroleum Technology', December 1966, B.R. Treadway, H. Brandt and P. Harold Parker, page 1537-1543, a three step sand consolidation process. Said process consisted of

- 25 (1) injecting epoxy resin
- (2) following the displacement of the resin by diesel oil to establish formation permeability, and
- (3) activating the resin to consolidate the formation by injecting an activator flush to cure the epoxy resin.

The applied epoxy resin system consisted of pure epoxy resin or an epoxy resin acid anhydride system.

Moreover it was known from '52nd Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME', Denver, Colorado, Oct 9-12, 1977, W.L. Penberthy, C.M. Shaugnessy, C. Gruesbeck and W.M. Salathiel (Exxon Production Research Co.), that for effective sand consolidation, the epoxy resin must wet the surface of the sand grains and that in those cases where the resins lack this ability a pre-flush which preferentially removes water in the presence of oil is essential and particularly when there had been a prior mud acid treatment. Radial field-scale model studies had demonstrated that pre-flush effectiveness was dependent on pre-flush volume, viscosity and sand permeability.

Due to the increased economic requirements for present exploitation of oil reservoirs, in incompetent, high temperature, high pressure formations said underground treating has to be further improved. By the term incompetent one will understand: formations of insufficient mechanical strength to allow sand-free production.

It will be appreciated that a clear disadvantage of the prior art underground treating methods was that the actual curing of the supplied epoxy resin and curing agent did not take place at the desired places due to high temperatures in the underground to be treated and/or the insufficient solubility or dispersability of the applied curing agents in the glycol ether solvent system or due to an unsuitable viscosity of the consolidation solution which caused that the required stoichiometric mutual ratio between epoxy resin molecules and curing agent molecules, could not be reached on the spot or in the specific area to be treated.

It will be appreciated that more in particular, consolidated formations should have the strength to withstand stresses induced by adjacent rock strata and stresses imposed by the flow of fluids into the wellbore. This consolidation strength should be maintained under production conditions, moreover the consolidated formation should have sufficient permeability to permit unobstructed flow of fluids into the wellbore and must show sufficient resistance to the conditions of well stimulation dilute solutions of acids, such as hydrochloric acid, hydrofluoric acid and acetic acid.

An object of the present invention is therefore to provide an improved method of treating hydrocarbon reservoirs in order to eliminate the entrainment of sand minerals and as a consequence wear of production equipment.

As result of extensive research and experimentation, such improved treating method has been surprisingly found.

Accordingly, the invention relates to a method of treating an underground formation of an oil reservoir in incompetent, high temperature, high pressure formations, comprising the sequential steps of

- a) contacting the formation with an aqueous medium,
- b) contacting the underground formation with a hydrocarbon fluid,
- 5 c) contacting the underground formation with a solvent in the form of a glycol ether,
- d) contacting the underground formation with a first consolidation constituent solution, mainly comprising a poly epoxy resin derived from bisphenols, or a poly phenolic resin (novolac resins), in a solvent mainly comprising a glycol ether, in an epoxy resin concentration of from 25 to 75%_m and having a viscosity in the range of from 10 to 100 m Pa.s ,
- 10 c) contacting the underground formation with a second constituent substantially homogenous consolidation solution mainly comprising a curing agent in a solvent, mainly comprising a hydrocarbon fluid. Said curing agent occurring in a concentration in the range of from 0.5 to 20 %_m, and the solution having a viscosity such, that the ratio between the viscosity of the solution in step (d) and of the solution in step (e) is in the range of from 1.0 to 5.

15 With the term 'mainly comprising' as used throughout the present specification is meant that the specified constituent (i.e. epoxy resin or solvent) is the sole component or can be mixed with minor amounts of co-components i.e. in amounts of 10 %_m or less and preferably in amounts of 5 %_m or less. For example, the preferably applied poly epoxy resin is a poly epoxy novolac resin, which optionally can be mixed with up to 10 %_m of a diglycidylether of diphenylolpropane (bisphenol A), or of
20 diphenylolmethane (bisphenol F).

The applied poly epoxy resin may be derived from phenol, cresols, xylenols, carvacol, cumenol and phenols, substituted with halogen or lower alkyl, having from 1 to 4 C atoms.

More preferably a poly epoxy phenol or cresol novolac resin is used of the type which is commercially available as EPIKOTE 154 (Traded by Resolution Performance Products).

25 The aqueous medium used in step (a) can be naturally occurring, treated i.e. filtered or desalinated water, such as pretreated sea water or water from rivers, or a KCl or NaCl brine, containing up to 6 %_m of KCl or NaCl, Na₂SO₄, K₂SO₄, NaNO₃, KNO₃ and the like and preferably up to 3 %_m and more preferably the same brine as originally occurring in the underground involved.

The hydrocarbon fluid, used in step (b) can be in principle selected from a great variety of
30 hydrocarbons but will be preferably selected from aliphatic hydrocarbons and more preferably gasoils .

The glycol ether solvent to be used in steps (c) and (d) can be selected from ethers of a C₂ to C₆ dihydric alkanol, containing at least one C₁ to C₆ alkyl group.

Preferably mono ethers of dihydric alkanols, more preferably glycol ethers selected from the group including methoxypropanol, butoxyethanol, hexoxyethanol and the isomers of these glycol ethers, or mixtures thereof.

To adjust the viscosity of said solvent it may further contain a minor amount e.g. less than 10 %, of a polyethylene glycol or polyvinyl pyrrolidone, having an average molecular mass of about 400.

The curing agent to be used in the solution of step (e) can be selected from a great variety of usually applied curing agents for epoxy resins with the restriction that such curing agent must be completely

miscible in the applied hydrocarbon fluid in a sufficient degree in order to reach the required concentrations, that the curing agent does not produce low molecular byproducts during curing and that the finally cured epoxy resin on the spot has sufficient mechanical strength, i.e. between the individual mineral groups on almost only on contact areas and must show a minimal impediment to fluid flow at the curing conditions on the spots to be treated, i.e. high temperature (from 80 to 200°C) and high pressure (from 10 to 100 atm).

Preferably amine type curing agents will be used selected from aliphatic di or poly amines or alkylaryl amines, more preferably diethylene toluene diamine, diethylene xylene diamine, diethylene dianiline are used, of which diethylene toluene diamine is the most preferred.

The solvent to be used in the step (e) is a hydrocarbon mixture e.g. SHELLSOL D70, SHELLSOL TD, SHELLSOL D40, SHELLSOL LF (SHELLSOL is a Shell Trade mark), EXXSOL D70 EXXSOL 155/170, EXXSOL D220/230 (EXXSOL is a Exxon Mobil Trade mark) HYDRSOL 75/95 N, HYDROSOL 100/130 N (HYDROSOL is a Total Fina Trade mark). To ensure that the viscosity of the mixture in step (e) has a viscosity in excess of that used in step (d), a viscosifier may be used, for example lubricant oil such as VALVATA 460, SHELLVIS 50 (VALVATA & SHELLVIS are Shell Trade mark), Worm Gear Oil (Amoco Oil Co) , CYLESSTIC TK-460 (CYLESSTIC is a Exxon Mobil Trade mark) SENATE 460 SENAT is a Gulf Oil Co Trade mark) .

It will be appreciated that a catalyst has preferably to be applied for the efficient curing of the epoxy resin/curing agent on the spot to be treated. Suitable curing catalysts can be selected from salicylic acid and phosphine, phosphonium amine and ammonium catalysts, which are generally known in the art.

Said catalyst can be added in amounts of up to 1% relative to the weight of the total supplied solution either in step (d), i.e. premixed with the epoxy resin component, or can be added in step, i.e. premixed with the curing agent in a solvent, of which the latter embodiment is preferred.

It will be appreciated that such sand consolidation method could meet all the presently desired sand consolidation characteristics, as were specified herein before.

The invention is further illustrated by the following examples, however without restricting its scope to these embodiments.

Examples

To illustrate the effect of method of the present on the unconfined compression strength, several samples were made and subjected to treatments. For each test three samples were made of "METTET QUARTZ SAND" (96% of the grain diameters are in the range of from 63 to 180 μm and $D_{50} = 130 \mu\text{m}$) in a glass tube, each sample had a diameter of 3.5 cm and a length of 17 cm. After the sand had been placed in the tube the porosity, Φ (in %) was determined. The sand pack was flushed with butane to remove air, and thereafter the sand pack was flushed with an aliphatic hydrocarbon in which butane dissolves to remove the butane. The initial permeability, K_i (in Darcy), was determined.

To simulate formation conditions, the following fluids were injected (1) methoxypropanol, (2) brine (2% KCl); and (3) about 10 pore volumes of crude oil to establish irreducible water saturation.

The treatment according to the invention comprises contacting the samples filled with crude oil at irreducible water saturation in the following sequence: (a) contacting the sample with 2 pore volumes of a 2% KCl brine; (b) contacting the sample with 2 pore volumes of gasoil; (c) contacting the sample with 2 pore volumes of methoxypropanol; (d) contacting the sample with 1 pore volume of a consolidation solution of

Example A: 1 pore volume (pv) of 28.8% EPIKOTE 154 in methoxypropanol, followed by 4 pv of 3.7% DETDA in a hydrocarbon solution, consisting of 31.7% SHELLSOL D70 and 68.3% VALVATA460.

Example B: 1 pore volume (pv) of 62.0% EPIKOTE 828 in methoxypropanol, followed by 4 pv of 1.96% DETDA in a hydrocarbon solution, consisting of 31.7% SHELLSOL D70 and 68.3% VALVATA460.

Example C: 1 pore volume (pv) of 38.0% m:m EPIKOTE 154 in methoxypropanol, followed by 4 pv of 7.2% m:m DETDA in a hydrocarbon solution, consisting of 33.1% m:m SHELLSOL D70 and 66.9.3% m:m VALVATA460.

5 Example D: 1 pore volume (pv) of 38.0 %m:m EPIKOTE 154 in methoxypropanol, followed by 4 pv of 21.6% m:m DETDA in a hydrocarbon solution, consisting of 36.0% m:m SHELLSOL D70 and 64.0% m:m VALVATA460.

Comparative Example : 1 pore volume (pv) of 46.5% m:m EPIKOTE 828 and 13.5% MDA m:m in methoxypropanol, followed by 4 pv of a hydrocarbon solution, consisting of 31.7% m:m SHELLSOL D70 and 68.3% m:m VALVATA460

10 After the treatment the final permeability, K_e (in Darcy), and the unconfined compression strength, UCS (in bar), were determined. The results are summarized in Table 1 below .

	Φ , in %	K_i , in Darcy	K_e , in Darcy	UCS, in bar
Example A	40	4.54	4.51	180
Example B	40.4	4.34	4.30	106
Example C	40.5	4.44	4.15	157
Example D	40.4	4.73	4.28	73
<u>Comparative</u>	41.2	4.13	3.96	156

Table : 1 Results of the treatment

15 From the examples made according to the present invention one can appreciate that the Example treated according to the inventions has a higher permeability for an excellent to acceptable unconfined compression strength compared to the state of the art technology. Moreover it has been found that the drop of permeability for the sample treated according to the invention is lower than the one reported in the prior art.

CLAIMS

1. A method of treating an underground formation of an oil reservoir, comprising the sequential steps of
- 5 a) contacting the formation with an aqueous medium,
- b) contacting the underground formation with a hydrocarbon fluid,
- c) contacting the underground formation with a solvent in the form of a glycol ether,
- d) contacting the underground formation with a first consolidation constituent solution, mainly
- 10 comprising a poly epoxy resin derived from bisphenols, or a poly phenolic resin (novolac resins), in a solvent mainly comprising a glycol ether, in an epoxy resin concentration of from 25 to 75% and having a viscosity in the range of from 10 to 100 mPa.s.
- e) contacting the underground formation with second consolidation constituent
- substantially homogenous solution mainly comprising a curing agent in a solvent, mainly
- 15 comprising a hydrocarbon fluid. Said curing agent occurring in a concentration in the range of from 0.5 to 20 %m, and the solution having a viscosity such, that the ratio between the viscosity of the solution in step (d) and of the solution in step (e) is in the range of from 1.0 to 5.
2. Method according to claim 1, wherein the epoxy resin solution is selected from a solid or liquid (at 23 deg C) epoxy-novolac resin and more preferably a solid epoxy novolac resin.
- 20 3. Method according to claim 1, wherein the curing agent is selected from aliphatic polyamines, alkyl-aryl polyamines and more preferably diethylene toluene diamine (DETDA).

(May 2003)

ABSTRACT

A method of treating an underground formation of an oil reservoir, comprising the sequential steps of

5 (a) contacting the formation with an aqueous medium, (b) contacting the underground formation with a hydrocarbon fluid, (c) contacting the underground formation with a solvent in the form of a glycol ether; (d) contacting the underground formation with a first consolidation constituent solution, mainly comprising a poly epoxy resin, (e) contacting the underground formation with second consolidation constituent substantially homogenous solution mainly comprising a curing agent in a solvent.

10

This sheet is not of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International Application No.

Applicant's or agent's
file reference

BE.02.021 PCT

Date stamp of the receiving Office

Applicant

Resolution Research Nederland B.V. et al

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE

EURO 100,00 T

2. SEARCH FEE

EURO 945,00 S

International search to be carried out by

(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

Where items (b) and/or (c) of Box No. IX apply, enter Sub-total number of sheets } 13

Where items (b) and (c) of Box No. IX do not apply, enter Total number of sheets }

b1 first 30 sheets EURO 444,00 b1

b2 number of sheets in excess of 30 x fee per sheet = EURO 0,00 b2

b3 additional component (only if sequence listings and/or tables related thereto are filed in computer readable form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii):

400 x fee per sheet = b3

Add amounts entered at b1, b2 and b3 and enter total at B EURO 444,00 B

Designation Fees

The international application contains 94 designations.

5 x EURO 96 = EURO 480,00 D
number of designation fees payable (maximum 5) amount of designation fee

Add amounts entered at B and D and enter total at I EURO 924,00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) P

5. TOTAL FEES PAYABLE

EURO 1969,00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☒ authorization to charge
deposit account (see below)

☐ postal money order

☐ cash

☐ coupons

☐ cheque

☐ bank draft

☐ revenue stamps

☐ other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all receiving Offices)

☒ Authorization to charge the total fees indicated above.

☒ (This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.

☒ Authorization to charge the fee for priority document.

Receiving Office: RO/ EP

Deposit Account No.: 28090077

Date: April 15th '03 (GA 43073)

Name: van der STRAATEN J.A.

Signature: